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CONCRETE TECHNOLOGY CORPORATION

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1123 PORT OF TACOMA ROAD / TACOMA, WASHINGTON 98421 / (206) 383-3545

A STUDY OF THE USE OF A FLUID BY-PRODUCT IN CEMENT AND CONCRETE MANUFACTURE

for the

MONSANTO COMPANY

SEATTLE, WASHINGTON PLANT

by

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INTRODUCTION

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The Monsanto Company, Seattle Plant, is a producer of Vanillin, a material used in food flavorings and pharmaceuticals. A by-product of their production is a thixotropic solution of calcium lignosulfonate. Since calcium lignosulfonate is the base chemical composition of many admixtures used in the concrete industry, Monsanto desired to determine the viability of their by-product as such an admixture.

At present, Lone Star Industries, Inc. is using the by-product in their Seattle, Washington, Cement Plant. The by-product is added to the cement production process at the slurry line. It is blended with the raw materials for calcining. The addition of the by-product to the cement production process has not been shown to be detrimental to the cement, neither has it been shown to enhance any cement properties. This report details the results of a study to determine the effect of treatment of cement with the Monsanto by-product. It also reports the results of the use of the by-product as an admixture introduced into fresh concrete.

The study was conducted by Concrete Technology Corporation of Tacoma, Washington. Mr. Bruce E. Pallante, Senior Process Engineer, represented the Monsanto Company to Concrete Technology Corporation and was principal liaison.

SUMMARY AND CONCLUSIONS

Investigation of the lignosulfonate based by-product was elementary in scope, the purpose being to discern the effect of treatment, if any, upon the physical properties of concrete made with 1) cement manufactured using the by-product in the production process, and 2) concrete manufactured using the by-product as a water reducing admixture.

The investigations centered on defining changes in the concrete's strength, workability, and times of set. The strength evaluation was based upon compressive strength, tensile splitting strength, and elastic modulus of 4 by 8 in. cylinders produced over a range of cement contents and dosages of by-product. The effects on the properties of the fresh (plastic) concrete were determined by tests for density (unit weight), air content, slump, and time of initial and final set. All tests were in compliance with ASTM standards except time of set, which was simply an empirical observation.

Definitions of the properties tested are found on page 3.

The conclusion drawn from the study of the cement made with the by-product added to the raw cement materials is that the by-product is not detrimental to the finished cement. No evidence was shown of enhancement of any property of concrete. However, it may aid cement production by reducing water requirement for given viscosities in the slurry line. It may also help keep the slurry in suspension.

Further study of cement made with the by-product addition is recommended. Any future work should be conducted on cement from one production run, before and after the addition of the by-product. The present study used as the control, a cement produced several months previous to the introduction of the by-product into Lone Star's process. This was done because no other samples were available. The ramifications of this are explained under compressive strength test results.

The tests conducted with the by-product added to fresh concrete indicate the by-product has some capacity for changing the slump of plastic concrete. The change in slump was small, however, for the quantity of by-product used. Thus it is not as effective as admixtures presently used in the industry and shows no particular promise in its present formulation. If the trace solvents were removed, the base lignin would probably perform better. That question remains unanswered since it was beyond the scope of the investigation. There is also indication that large doses of the by-product may cause detrimental effects. These questions are discussed in the report under the heading of the property affected.

DEFINITIONS

Cement: A powder of alumina, silica, lime, iron oxide, and magnesia burned together in a kiln and finely pulverized and used as an ingredient of mortar and concrete.

Concrete: A hard strong building material made by mixing a cementing material (as portland cement) and a mineral aggregate (as sand and gravel) with sufficient water to cause the cement to set and bind the entire mass.

Compressive Strength: The measured maximum resistance of a concrete specimen to axial loading, expressed as force per unit cross sectional area. It is the specified resistance used in design calculations. In the United States, it is expressed in pounds per square inch (psi) and designated f'_c. Standard Method of Test, ASTM C 39.

Tensile Splitting Strength: The maximum resistance of a concrete cylinder specimen to diametrical compression stresses, the ability to withstand being pulled apart. Standard Method of Test, ASTM C 496.

Density: The mass per unit volume of concrete, expressed in the United States as pounds per cubic foot (pcf). Standard Method of Test, ASTM C 138.

Slump: A measure of consistency of freshly mixed concrete equal to the subsidence measured to the nearest 1/4 in. of a molded truncated cone. The mold is in the form of the lateral surface of the frustrum of a cone with the base 8 in. in diameter, the top 4 in. in diameter, and the height 12 in. Standard Method of Test, ASTM C 143.

Air Content: The volume of air voids in cement paste or concrete, exclusive of pore space in aggregate. Usually expressed as a percentage of total volume of the paste or concrete. Standard Method of Test, ASTM C 231.

Time of Set: A degree of stiffening of concrete generally stated as an empirical observation indicating the time in hours and minutes required for concrete to stiffen sufficiently to resist penetration by laboratory penetrometers. Standard Method of Test, ASTM C 403.

Elastic Modulus: The ratio of normal stress to corresponding strain for tensile or compressive stresses below the proportional limit of the material. The modulus is expressed as pounds of force per unit of area (psi) in the United States. Standard Method of Test, ASTM C 469.

PART I

Cement with By-product/Cement Without

INVESTIGATION FORMAT

This experiment compared concretes made with type III cement in which the Monsanto by-product was used in the manufacturing process (hereinafter referred to as cement or concrete "M") to a cement without the by-product (hereinafter referred to as cement or concrete "C").

Two control concretes were produced containing 4.5 and 6.5 sacks per cubic yard of cement C. Two additional batches of concrete were produced at the same cement content using cement M. The four batches were compared for unit weight, air content, and slump. Six 4 by 8 in. test cylinders and two 6 by 12 in. cylinders were molded from each of the four batches and tested for strength at 1, 7, and 28 days maturity. The strength specimens were ambient cured for 24 hours before removing from molds. After mold removal, the specimens were stored in 73 deg F lime-saturated water until time of test.

TEST RESULTS

A. Compressive Strength

Compressive test results of the 4 by 8 in. cylinders indicate the concrete made with cement M is not of the same quality as concrete made with cement C. At 28 days age and 4.5 sack cement content level, concrete C developed 900 psi more than concrete M, a substantially higher figure. The 28 day results of the 6.5 sack mixes were somewhat better with concrete C developing only 460 psi greater strength. However, at the earlier ages of 1 and 7 days, concrete M outperformed concrete C.

It is suspected the two cements vary in their tricalcium silicate and/or tricalcium aluminate content. Examination of the cement mill certificate does not reveal any large variations in the potential compound composition of the cement utilizing the by-product. These chemical compounds contribute the most to early strength development.

However, it should be emphasized that the potential compound compositions reported on mill certificates are only calculations and not measurements. As such, they give only rough indications of the amounts of various minerals present in cement. For reasons which are not yet fully understood, the actual mineralogical composition of portland cement can differ appreciably from that given by calculations. It is also emphasized that very small changes in raw materials can produce large effects in the properties of the finished cement. Thus, it is possible for two cements with nearly identical mill certificates to differ markedly in their rate of strength development.

The early strength advantage demonstrated by concrete M may be attributable to the above. The 28 day strength, though less than the control concrete, is quite satisfactory. Strength data are presented in Table I. Figure I presents a graph of the results. Cement mill certificates are appended.

B. Tensile Splitting Strength

Tensile splitting strengths for concrete M are comparable to those found for concrete C. The small differences are quite probably due to the vagaries of sampling and testing. The data are found in Table 2. Results are graphed in Figure I.

TABLE I

Compressive Strength

	I Day	7 Days		28 Days	
	Individual (psi)	Individual (psi)	Average (psi)	Individual (psi)	Average (psi)
4.5 sack cement C	1310	6610 6730	6670	8440 8240	8340
4.5 sack cement M	1430	6010 6010	6010	7520 7360	7440
6.5 sack cement C	1950	8800 8960	8880	10590 10470	10530
6.5 sack cement M	2990	9310 9160	9240	10430 9710	10070

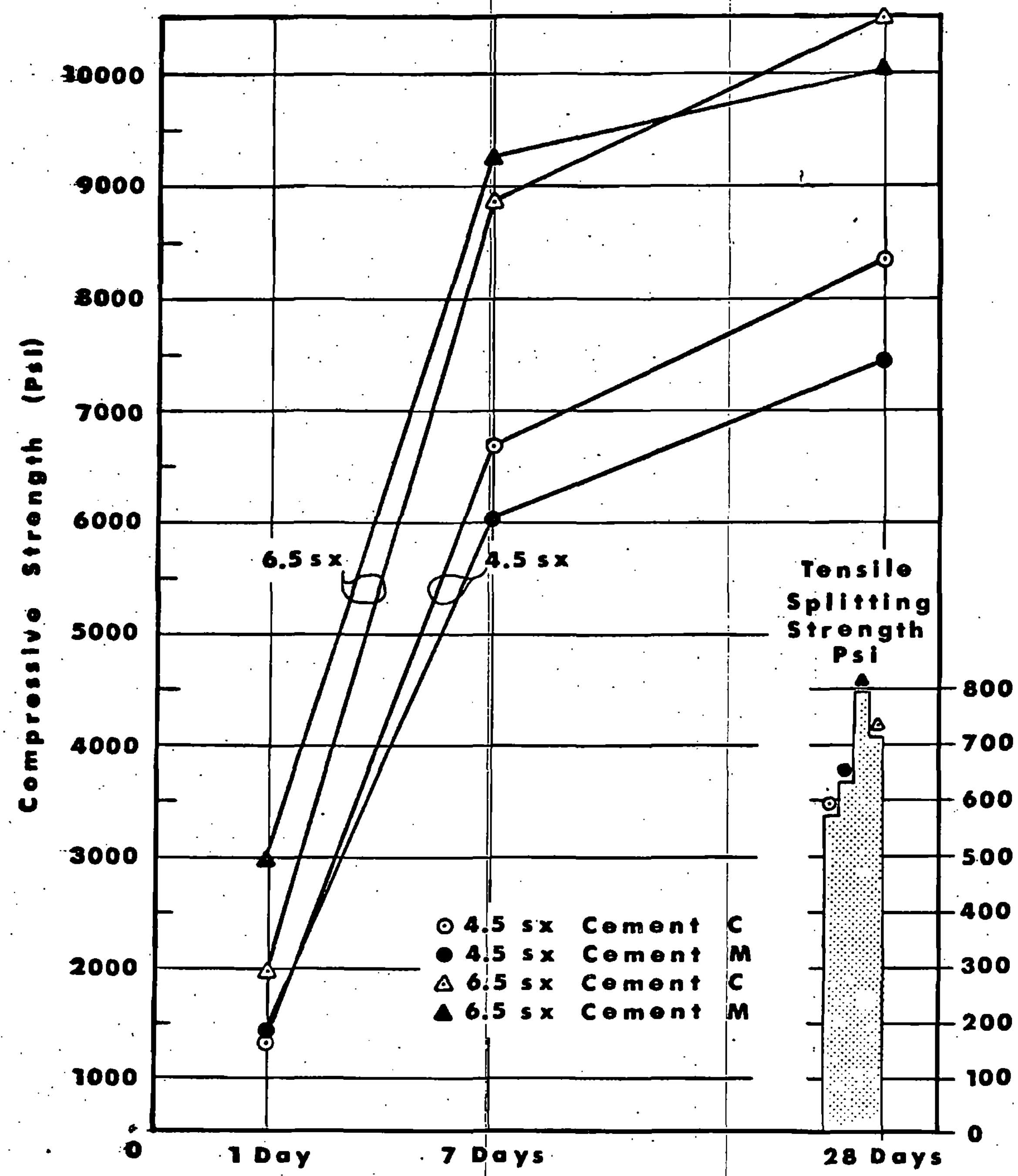
Compressive Strength (Psi)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
6.5 sx
4.5 sx
Tensile Splitting Strength Psi
800
700
600
500
400
300
200
100
0
4.5 sx Cement C
4.5 sx Cement M
6.5 sx Cement C
6.5 sx Cement M
1 Day
7 Days
28 Days

Figure I

TABLE 2

Tensile Strength

4.5 sack cement C	570 psi
4.5 sack cement M	630 psi
6.5 sack cement C	710 psi
6.5 sack cement M	790 psi

C. Density

The mass per unit volume of concrete produced with both cements at two cement content levels was normal in both the plastic (wet) and hardened states. There was no indication of variation in density due to addition of the by-product to the cement manufacturing process. The density data are found in Table 3.

D. Slump

The plasticity of the fresh concrete was as expected with no difference noted between the two cements at either cement content level. Slump data are found in Table 3.

E. Air Content

Air content tests were conducted on all four batches of concrete using ASTM C 213-75, Pressure Method. No significant deviations from normal were expected or found. Data are located in Table 3.

F. Time of Set

All batches of concrete displayed normal set times for type III cement. No difference was apparent between the conventional cement and the by-product treated cement or between cement content levels.

Data are located in Table 3.

TABLE 3

Cement Content	Density Wet	Density Hard	Slump	Air (percent)	Time of Set
4.5 sx C	155.21	156.0	1.25 in.	1.6%	2 hrs 10 min
4.5 sx M	155.9	153.5	1.25 in.	1.5%	2 hrs
6.5 sx C	155.9	155.5	1.0 in.	1.8%	2 hrs
6.5 sx M	155.2	154.3	1.0 in.	1.1%	2 hrs 15 min

PART II

Use of By-product as Admixture

INVESTIGATION FORMAT

Four batches of concrete were produced using the same mix design (proportions). The only variable was the amount of by-product added to the concrete. The mix design (proportions) used is appended. The addition rates of by-product per 94 lb sack of cement were 0 oz, 8 oz, 16 oz, and 32 oz. The treated specimens were compared to the zero dosage control specimen. After measuring unit weight, slump, and air content of the fresh concrete, six 4 by 8 in. cylinders and two 6 by 12 in. cylinders were cast and stored in a saturated lime-water solution in accordance with ASTM C 192-69 and tested at 1, 7, and 28 days maturity.

TEST RESULTS

A. Compressive Strength

Compressive strength of the concrete made with the by-product added at 3 dosage levels indicated the material does not aid and, in large quantities, may be detrimental to concrete strength development. All concretes containing the by-product tested equal to or less than the control concrete. The control specimen at 28 days tested at 9,120 psi. The 8 and 16 oz dosages of by-product yielded 8,840 and 9,160 psi, respectively. The apparently equal strengths were felt to be from the same population of strength values as the control specimen. The 32 oz treatment yielded only 8,060 psi, approximately 1,000 psi less than the control, 8, and 16 oz treatments. The concrete containing 32 oz of by-product per sack of cement displayed a glossy, bubbly appearance indicating a reaction with the cement. This reaction appeared to be generating gas, leaving the matrix with numerous voids. These voids are believed to account for the lower strength.

A concrete producer using the by-product at the 32 oz per sack treatment level would have to use at least one sack of cement more to achieve the same strength as concrete without the by-product. Thus, no strength benefit is demonstrated from the use of the by-product and a question is raised regarding possible detrimental effects with large treatments.

The strength data are found in Table 4 and graphed in Figure 2.

B. Tensile Splitting Strength

Split tensile tests indicate the tensile strength of treated concrete remained unchanged except at the 32 oz per sack treatment level. The split tensile strength of that specimen was 26 percent lower than the control, 8, and 16 oz per sack treatments. The split matrix displayed large voids when compared to the other specimens. Tensile splitting data are found in Table 5 and graphed in Figure 2.

C. Densities

The fresh unit weights of the plastic concrete were normal in all cases. The hardened unit weights were determined after immersion in lime-saturated water for 28 days. That condition makes possible the measurement of the concrete's heaviest weight. The concretes with 0, 8, and 16 oz doses of by-product responded normally with slight increases in mass due to absorption. The concrete with the 32 oz dose of by-product apparently absorbed very little water. The lighter unit weight of the 32 oz treatment corresponds closely with its lighter wet unit weight but the concrete actually lost mass during the interim. This is believed due to the presence of many voids in that specimen. These voids apparently have an impermeable wall so that they remained unfilled during the soaking period. That raises the possibility that the by-product in large dosages may tend to enhance impermeability of concrete. That question bears further investigation. The unit weight and graph are found in Table 6 and Figure 3.

TABLE 4

Compressive Test Results

	1 Day	7 Days		28 Days	
	Individual (psi)	Individual (psi)	Average (psi)	Individual (psi)	Average (psi)
Control Concrete	1590	7560 7560	7560	9390 8840	9120
8 oz/sx by-product	1630	7370 6800	7060	8480 9200	8840
16 oz/sx by-product	1790	7160 7400	7280	9270 9040	9160
32 oz/sx by-product	1790	6760 6960	6860	8520 7600	8060

TABLE 5

Tensile Splitting Tests

	28 Days
Control concrete	690 psi
8 oz/sx by-product	600 psi
16 oz/sx by-product	640 psi
32 oz/sx by-product	510 psi

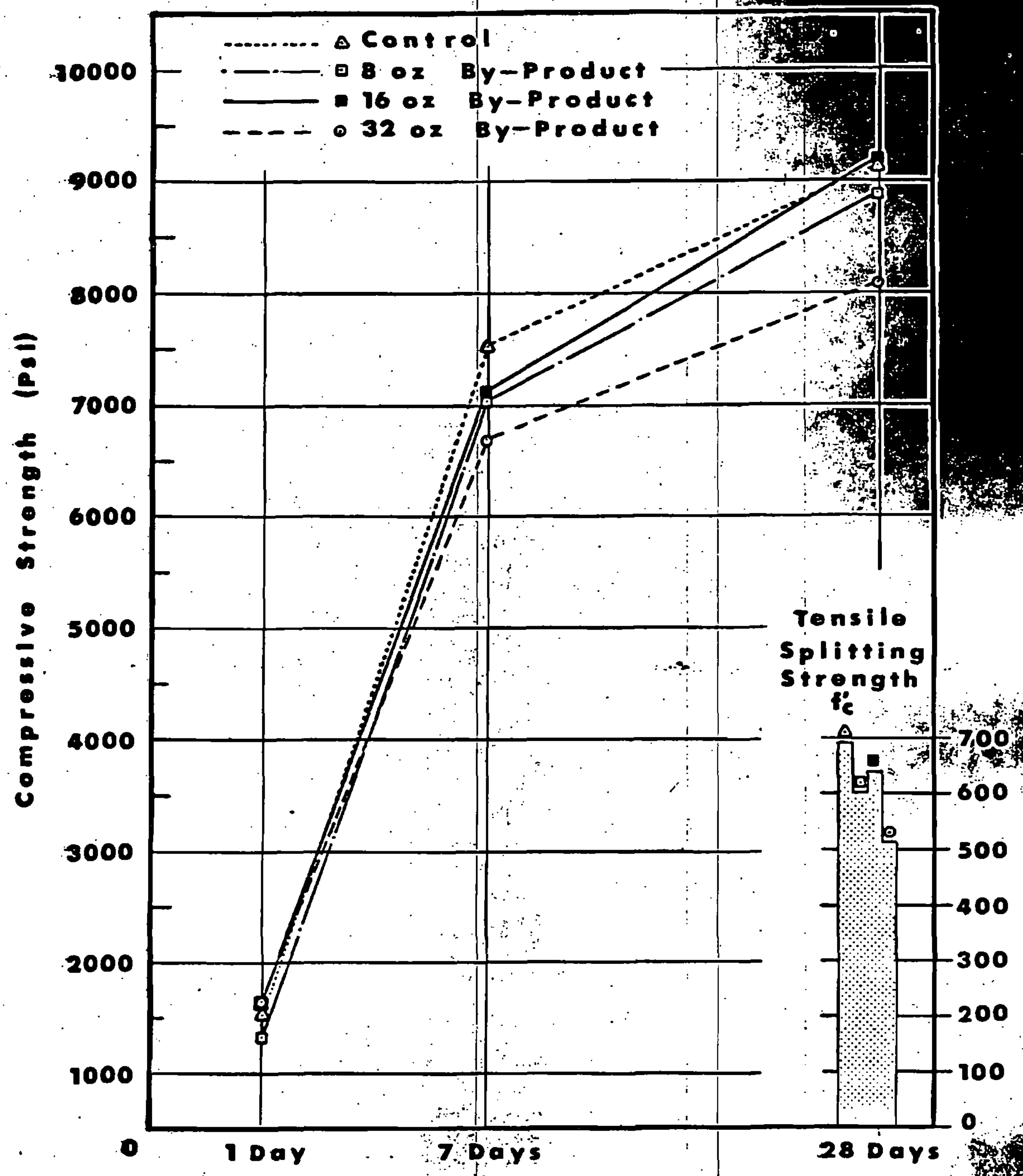
Control
8 oz By-Product
16 oz By-Product
32 oz By-Product
Compressive Strength (Psi)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1 Day
7 Days
28 Days
Tensile Splitting Strength f'c
700
600
500
400
300
200
100
0

Figure 2

TABLE 6

Concrete Density (pcf)

	Wet	Hardened
Control	150.88	151.07
8 oz/sx by-product	150.88	152.3
16 oz/sx by-product	150.88	152.65
32 oz/sx by-product	151.87	151.4

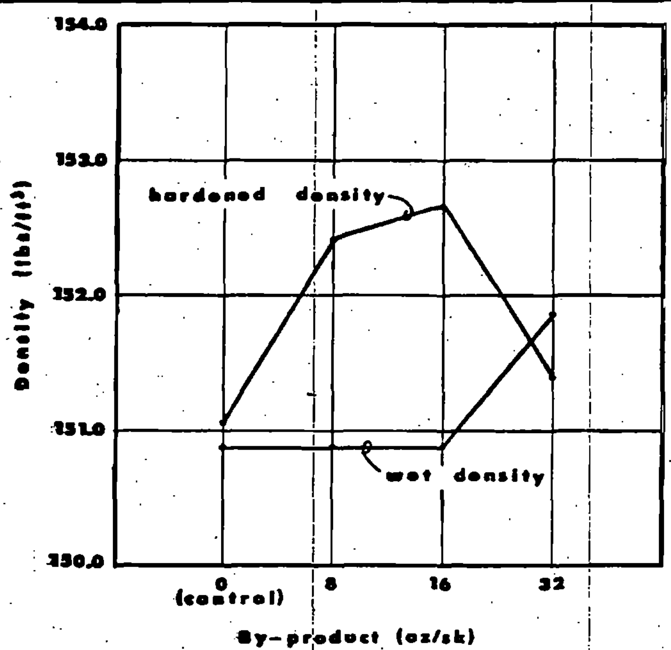

Figure 3

D. Slump

Increasing dosage levels of by-product at fixed water contents increases the slump, or plasticity, or fresh concrete through the normal range of usage. Doubling the dosage increases the slump linearly through 16 oz per sack of cement. At the 32 oz treatment level the relationship departs from linearity with the concrete displaying a glossy, bubbly consistency. These tests indicate the possibility of using the by-product as an ASTM Typ e A water reducing admixture if the material can be shown compliable to ASTM C 494. A copy of this standard is appended. Slump data and graph are found in Table 7 and Figure 4.

TABLE 7

Slump

Control	3.25 in.
8 oz/sx by-product	4.5 in.
16 oz/sx by-product	5.5 in.
32 oz/sx by-product	7.5 in.

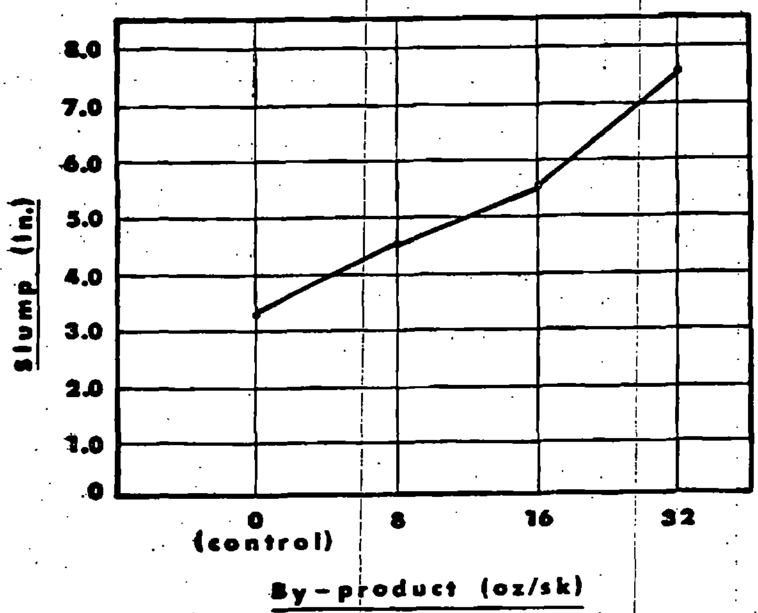

Figure 4

E. Air Content

The air content of the trial batches was determined using a pressure meter. The mix design assumed 2 percent air entrapped in the matrix. Since no air entraining agent was used, air contents larger than 2 percent were deemed attributable to the by-product. Results indicate the by-product entrains air linearly through the 16 oz per sack treatment level. At the 32 oz per sack level the air content was twice as much as the 16 oz per sack level. The concrete containing 32 oz per sack had a very glossy, bubbly appearance indicating an increased level of air or gas. The air content test confirmed this by measuring 4 percent. Although this is not in the detrimental range, if used with other air entraining agents such as vinsol resin, it could possibly be difficult to control the amount of air generated. The air content data are found in Table 8 and Figure 5.

TABLE 8

Air Content

	Percent Air
Control	1.5
8 oz/sx by-product	1.75
16 oz/sx by-product	2.0
32 oz/sx by-product	4.0

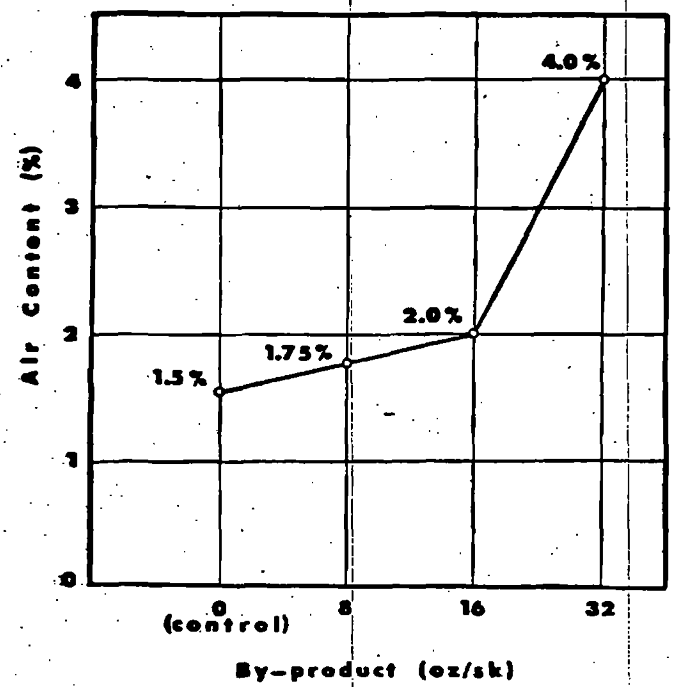

Figure 5

F. Time of Set

All trial batches revealed setting times of approximately 2 hours 5 minutes, well within the working range of 2 to 3 hours.

G. Elastic Modulus

The elastic modulus of the concrete made with by-product is in the normal range of 3.5×10^6 psi to 6.0×10^6 psi. Test results are found in Table 9.

TABLE 9

Elastic Modulus

Control - No By-Product	Modulus (psi)
8 oz treatment	4.9×10^6
16 oz treatment	5.5×10^6
32 oz treatment	4.3×10^6

H. Leachates

After compressive testing, the ruptured cylinder specimens were immersed in water for observation of leachates. Particular attention was given to inspection for discoloration or unusual leaching as evidenced by crystalline growth on the exposed surfaces of ruptured cylinders. No leaching was observed and no change in pH of the water was noted.

APPENDIX

Mix Designs (proportions)

A. 6.5 sack design for cement with by-product/cement without

B. 4.5 sack design for cement with by-product/cement without

C. 6.0 sack design for use with increasing quantity of by-product

D. ASTM-C494, Standard Specifications for Chemical Admixtures for Concrete

E. Cement Mill Certificates

CONCRETE TECHNOLOGY CORPORATION

MONSANT[illegible]Y-PRODUCT TESTS
FOR USE WITH CEMENT C AND M
(6.5 sx)

1123 PORT OF TACOMA ROAD / TACOMA, WASHINGTON 98421 / (206) 383-3545

CONCRETE MIX DESIGN

ITEM	CEMENT	SAND	FINE AGGREGATE	COARSE AGGREGATE	WATER	AIR	TOTAL
SSD WEIGHT	611	1325		1987	30 gal 250	1½%	4173
PERCENT AGGREGATE WEIGHT		40		60			
SPECIFIC GRAVITY	3.15	2.72		2.73			
ABSOLUTE VOLUME	3.11	7.80		11.7	4.01	0.41	27.0
MOISTURE CONTENT							
ABSORPTION PERCENT		>1.0		>1.0			
CORRECTION PERCENT							
CORRECTION POUNDS							
BATCH WEIGHTS							

GRADATION - PERCENT PASSING

3"	1½"	1"	3/4"	1/2"	3/8"	5/16"	#4	#8	#16	#30	#50	#100	#200

CONCRETE TECHNOLOGY CORPORATION

MONSANTO BY-PRODUCT TESTS
FOR USE WITH CEMENT C AND M
(4.5 sx)

1123 PORT OF TACOMA ROAD / TACOMA, WASHINGTON 98421 / (206) 383-3545

CONCRETE MIX DESIGN

ITEM	CEMENT	SAND	FINE AGGREGATE	COARSE AGGREGATE	WATER	AIR	TOTAL
SSD WEIGHT	423	1391		2086	30 gal 250	1½%	4150
PERCENT AGGREGATE WEIGHT							
SPECIFIC GRAVITY							
ABSOLUTE VOLUME	2.15	8.19		12.25	4.01	0.41	27.0
MOISTURE CONTENT							
ABSORPTION PERCENT		>1.0		>1.0			
CORRECTION PERCENT							
CORRECTION POUNDS							
BATCH WEIGHTS							

GRADATION - PERCENT PASSING

3"	1½"	1"	3/4"	1/2"	3/8"	5/16"	#4	#8	#16	#30	#50	#100	#200

CONCRETE TECHNOLOGY CORPORATION

MONSA[redacted]O BY-PRODUCT
FOR USE AS BASE DESIGN
IN TESTS AS ADMIXTURE

1123 PORT OF TACOMA ROAD / TACOMA, WASHINGTON 98421 , (206) 383-3545

CONCRETE MIX DESIGN

ITEM	CEMENT	SAND	FINE AGGREGATE	COARSE AGGREGATE	WATER	AIR	TOTAL
SSD WEIGHT	6 sx 564	1333		1999	31.0 8.33 258	1½%	4154
PERCENT AGGREGATE WEIGHT		40		60			
Density SPECIFIC GRAVITY	3.15	2.72		2.73	1.0		
ABSOLUTE VOLUME	2.87	7.85		11.73	4.13	0.41	26.99
MOISTURE CONTENT							
ABSORPTION PERCENT		<1.0		<1.0			
CORRECTION PERCENT							
CORRECTION POUNDS							
BATCH WEIGHTS							

GRADATION - PERCENT PASSING

3"	1½"	1"	3/4"	1/2"	3/8"	5/16"	#4	#8	#16	#30	#50	#100	#200
				94	64	---	42	32	24	15	5	1	